Energy 45 (2012) 746–752

Contents lists available at SciVerse ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Determination of the specific heat of biomass materials and the combustion energy of coke by DSC analysis

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ARTICLE INFO

Article history:
Received 9 December 2011
Received in revised form
27 June 2012
Accepted 7 July 2012
Available online 4 August 2012

Keywords:
Solid biofuel
Sampling methodology
Uncertainty
Specific heat
DSC analysis

ABSTRACT

The accurate determination of the thermal properties of biomass materials is particularly important when studying biomass combustion processes. This paper reports a method for the determination of the maximum sampling error and the confidence intervals of thermal properties obtained from TG–DSC analysis. Special care must be taken with the sampling procedure to achieve an acceptable degree of error and low statistical uncertainty. The obtained levels of uncertainty and error demonstrate that the properties evaluated by the analysis were representative of the fuels. A study of the trends and time correlations was performed to ensure that the observed correlations arise from completely random causes. The obtained results are particularly interesting for biomass energy applications.

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1. Introduction

Global concern about environmental protection grew considerably in the last few decades to culminate in the Kyoto Protocol [1], which set major directives and acceptable pollutant emission levels. The participants in the 2009 United Nations Climate Change Conference recognized that climate change is one of our primary challenges and that actions should be taken to avoid any global temperature increases. The Kyoto protocol, which expires in 2012, was ratified at the Copenhagen Summit so that its policies may be continued; however, no agreement was reached with respect to emissions reductions beyond 2012, and the final agreement is not legally bound. After the ratification of the Kyoto Protocol, considerable efforts have been made to measure and control pollutant output from all energy processes and especially to minimize greenhouse gases. The development of renewable, clean energies such as biomass has become an important working area as part of the proposed action plan [2,3]. Biomass cofiring has, in fact, become one of the most worthwhile methods to reduce pollutant emissions from energy-production processes because the adjustments required to power plants entail low costs [4–6].

Several different technologies are normally applied in cofiring processes [7]. The main advantages of each technology have been highlighted by various authors [4,5,7–12]. Cofiring can help to reduce specific emissions of CO_2 because of the closed carbon cycle; the low sulfur content of the biomass helps minimize SO_2 emissions, and NO_x emissions also show a positive trend. Cofiring increases the operational flexibility of the process, which reduces dependence on fossil fuels, such as coal. However, the main drawbacks of this technology are the additional cost of adapting combustion facilities and the increased fouling and corrosion of equipment [7].

Knowledge of the chemical composition, thermal behavior and reactivity of biomass is essential for the effective design and operation of thermochemical conversion units [13]. Thermoanalytical techniques, such as thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), provide this information in a straightforward manner [14–18]. TG analyses are based on the volatilization rate of fuels, which is dependent on the heating rate applied to the sample and the type of fuel. DSC, in contrast, is based on measurements of the energy change of the sampling unit under a predetermined heat cycle [19,20].

The intrinsic heterogeneity of the biomass and the small amount of sample used in TG/DSC experiments makes it difficult to determine the thermal properties accurately. Therefore, to determine the characteristics of the biomass with an acceptable, clearly defined level of uncertainty, a well-defined TG/DSC method must be

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http://dx.doi.org/10.1016/j.energy.2012.07.018

developed. Many studies on the accuracy of TG/DSC experiments have been published [21–25], and various sampling methods have been proposed [26,27]. Currently, TG/DSC methodologies are often based on small samples obtained from large batches; thus, careful reduction is necessary to prevent segregation and stratification problems [24]. In general, a good sampling method should be able to achieve a representative sample without being affected by the aforementioned problems.

A new methodology for the sampling of solid biomass, including the determination of error associated with the measurement of thermal properties, has been presented and validated [28–31]. This method is independent of the origin, appearance and packaging of the batch used to acquire the samples.

The statistical uncertainty associated with eight different properties of solid fuels, which has been calculated from moisture and ash tests, was presented in [30]. The values obtained show that despite the heterogeneity of the fuel itself, a well-planned campaign of samples can extrapolate the properties of the samples from the entire lot with an uncertainty controlled and quantified.

A methodology for prompt analysis of heterogeneous solid fuels was developed taking special care with the sampling procedure to achieve an acceptable degree of error and low statistical uncertainty [31]. Two approaches for the propagation of errors are also given and some comparisons are made in order to determine which may be better in this context. Acceptable levels of uncertainty were reached demonstrating that the samples obtained in the process are representative of the overall fuel composition.

The determination of the maximum sampling error and confidence intervals of thermal properties obtained from thermogravimetric analysis (TG), including moisture, volatile matter, fixed carbon and ash content was studied [28,29]. The results of the previous studies were compared to those of a prompt analysis, and a correlation between the mean values and maximum sampling errors of the methods were not observed. In general, low and acceptable levels of uncertainty and error were obtained with this methodology, demonstrating that the properties evaluated by TG analysis were representative of the overall fuel composition.

In the present study, the error associated with the aforementioned methodology and the confidence intervals of the specific heat of dry biomass and coke were determined, along with the heat of combustion of coke. The overall uncertainty of the measurements was defined, which allowed us to determine the minimum number of samples necessary to achieve an acceptable level of reliability. A comparative study on the mean values of the thermal properties and the corresponding uncertainties in TG experiments was conducted [28,29], and a relationship was not observed. Moreover, the confidence level and error associated with the measurement of thermal properties were not well correlated.

2. Experimental section

All materials were handled under the same conditions; they were tested in the same laboratory by the same analyst. Although the materials were exposed to environmental conditions for a short period of time (less than 30 min) during their manipulation, the effects of environmental variations in the properties of the materials were not taken into account because the variations in temperature and relative humidity were insignificant over such a short time period.

Laboratory instruments were verified and calibrated to assure that the experimental methodology was accurate. Errors registered during the experiments were considered to be random errors and were related to the precision of the experiment. Thus, these errors were quantified in the total sampling error.

2.1. Materials

Several different materials from agriculture and forestry were selected for the study. The materials cover a broad spectrum of solid biomass that could be used as fuel in cofiring processes. The agricultural materials were stored in large bags, and the forestry materials, in pellet form, were stored in sacks. The materials of agricultural origin were pine kernel shells, almond shells, hazelnut shells and ground olive stones. The materials of forest origin were pine pellets, oak pellets, brassica pellets and poplar pellets.

2.2. Sampling and reduction of the samples

Depending on the material, the sampled masses varied from $320 \cdot 10^{-3}$ kg to $730 \cdot 10^{-3}$ kg. Fuel samples were obtained from a tube sampler that was designed according to the requirements specified in CEN/TS [32] and the work of Pierre Gy [33–35]. The sampling methodology used to obtain the fuel sampling units and the method used to reduce the samples are described elsewhere [28–31]. Fuel samples were obtained through a tube sampler that was designed to work with various types of solid biomass. The nominal maximum size, d, of the material sampled is taken as 20 mm [31], so the tube sampler should be able to collect at least $V_{\min} = 0.05 \cdot d = 0.05 \cdot 20 = 1\ \mathrm{dm}^3 = 10^{-3}\ \mathrm{m}^3$ [31]. Table 1 shows the average weight of the sampling units selected for TG/DSC analysis. Tweezers were used to place the sampling units into the crucibles.

2.3. TG/DSC analysis methodology

All TG/DSC experiments were performed on a TG-DTA/DSC SETARAM Labsys electronic thermobalance, which can achieve a maximum temperature of 1600 °C and heating rates from 0.001 to 50 $^{\circ}\mathrm{C\ min}^{-1}$. To avoid heat- and mass-transfer limitations, approximately $20 \cdot 10^{-6}$ kg of sample was used, and platinum crucibles without lids were employed. All experiments were initially conducted under a flow of nitrogen at a rate of 45 $\mathrm{mL\ min}^{-1}$ to avoid oxidation of the sampling elements. After a temperature of 600 °C was reached, dry air was introduced instead of nitrogen to allow an estimation of the heat of combustion of the coke that remained in the container. The temperature cycle and gas employed at each temperature are shown in Table 2. At the beginning of the tests, all of the equipment and sampling units were in thermal equilibrium at 30 °C.

Moisture, volatile, char and ash content can be by determined TG/DSC results [28,29], but the main objective of this paper is to determine the thermal properties of the studied materials, including the specific heat (c_p) of the dry biomass and coke and the heat of combustion of the coke.

The TG curve obtained is shown in Fig. 1, which also shows the DSC curve. The TG curve represents the evolution of the mass as a function of the temperature. The DSC curve allows the calculation

Table 1
Average weights of the sampling units selected for the tests.

Material	Sampling unit weight [kg]
Almond shell (As)	21.53×10^{-6}
Ground olive stone (Gos)	22.44×10^{-6}
Oak pellets (Op)	21.44×10^{-6}
Pine Pellets (Pin)	20.70×10^{-6}
Hazelnut shell (Hs)	21.29×10^{-6}
Pine nut shell (Pns)	21.98×10^{-6}
Poplar pellets (Pp)	22.46×10^{-6}
Brassica pellets (Bp)	21.18×10^{-6}

Table 2
Thermal evolution of the samples in the TG/DSC tests.

T_{start} [°C]	T_{end} [°C]	SR [°C min^{-1}]	Time [s]	Atmosphere
30	70	30	80	N_2
70	90	15	80	N_2
90	105	2	450	N_2
105	105	0	1800	N_2
105	145	10	240	N_2
145	145	0	600	N_2
145	500	10	2130	N_2
500	500	0	3600	N_2
500	600	20	300	N_2
600	600	0	600	N_2
600	600	0	2400	Air
600	700	20	300	Air
700	700	0	600	Air

of the flow of energy by integrating the surfaces of the positive or negative peaks for exothermic or endothermic processes, respectively.

The energy absorption is calculated from the analysis of the endothermic peaks that occur during the test between 105 °C and 145 °C for the dry biomass and between 500 °C and 600 °C for the coke. The following Equation (1) allows the calculation of the specific heat (c_p) of dry biomass and coke for every presented material:

$$\frac{dH}{dt} = mc_p\frac{dT}{dt}. \tag{1}$$

The energy of coke combustion is provided by the analysis of the exothermic peak that occurs in the vicinity of 600 °C when dry air is supplied instead of nitrogen to begin the combustion process. Specific values are obtained by taking into account the loss of mass during the process.

2.4. Statistical treatment

2.4.1. Measured variable error

According to Gy [33], the batch to be sampled can be considered as a zero-dimensional object. Using the previously described sampling procedure, a sample of the total batch was chosen. Assuming that the sampling procedure is correct, the sampling error, SE, can be expressed as the sum of two components: the fundamental error, FE, and the segregation and grouping error, SGE. Moreover, because these two errors are independent, the following relationship between their variances holds:

$$\sigma^2(\mathrm{SE}) = \sigma^2(\mathrm{FE}) + \sigma^2(\mathrm{SGE}). \tag{2}$$

The FE is related to the constitutional heterogeneity; it is never zero, and it represents the minimum sampling error that can be made. The variance of the fundamental error can be expressed as:

$$\sigma^2(\mathrm{FE}) = \left(\frac{1}{M_m} - \frac{1}{M_L}\right)HI_L, \tag{3}$$

where M_m is the sample mass, M_L is the mass of the whole batch and HI_L is the heterogeneity invariant given by:

$$HI_L = \frac{1}{N_F}\sum_{i=1}^{N_F}\left(\frac{a_i - a_L}{a_L}\right)^2 M_i, \tag{4}$$

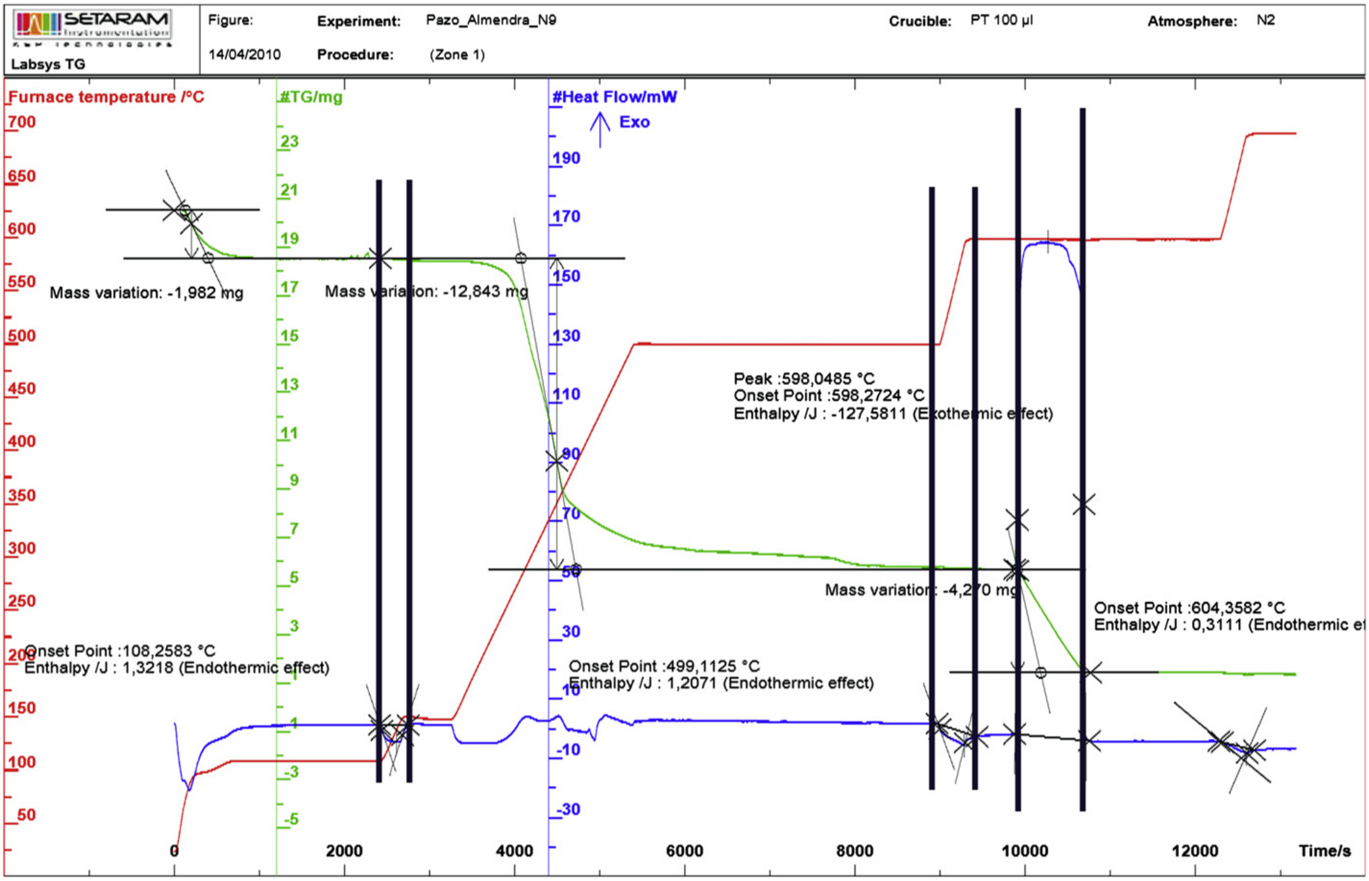

Fig. 1. The obtained DSC and TG curves.

Table 3
Values obtained from the TG/DSC analysis for $c_{p,db}$ [J g^{-1} K^{-1}], $c_{p,ck}$ [J g^{-1} K^{-1}] and h_{comb} [kJ g^{-1}].

		Sampling unit										Mean	S^2
		#1	#2	#3	#4	#5	#6	#7	#8	#9	#10		
As	$c_{p,db}$	1.265	1.360	1.469	1.559	1.470	1.475	1.322	1.853	1.806		1.509	0.041
	$c_{p,ck}$	2.345	2.373	2.018	2.468	2.370	2.138	–	2.608	2.840		2.395	0.066
	h_{comb}	29.892	27.710	30.328	29.149	27.711	27.749	29.638	29.602	29.878		29.073	1.121
Bp	$c_{p,db}$	1.798	1.353	1.506	1.371	1.419						1.489	0.033
	$c_{p,ck}$	2.712	1.916	3.130	2.319	2.299						2.475	0.213
	h_{comb}	33.494	29.690	28.991	30.810	28.236						30.244	4.197
Gos	$c_{p,db}$	2.158	2.334	0.678	1.133	1.150	1.351	2.232	2.241	2.378		1.739	0.428
	$c_{p,ck}$	2.943	2.622	–	0.800	–	–	2.775	2.814	2.577		2.422	0.649
	h_{comb}	25.383	27.000	25.457	25.574	26.125	26.334	26.404	26.815	27.339		26.270	0.494
Hs	$c_{p,db}$	1.680	1.715	1.612	1.630	1.801	1.697	1.645	1.799	1.837		1.713	0.007
	$c_{p,ck}$	0.858	3.298	2.643	2.922	2.634	2.199	2.185	2.158	3.093		2.443	0.523
	h_{comb}	32.849	32.540	31.178	31.661	30.841	31.370	29.792	29.934	28.948		31.012	1.653
Op	$c_{p,db}$	2.691	2.920	2.748	2.986	3.268	2.852	2.863	2.838	2.243	2.236	2.764	0.101
	$c_{p,ck}$	–	5.565	4.494	4.299	4.990	4.067	3.891	4.147	3.327	–	4.348	0.470
	h_{comb}	27.615	27.551	27.904	27.670	27.613	27.736	26.707	26.990	25.570	25.228	27.058	0.901
Pin	$c_{p,db}$	1.698	1.845	1.904	1.762	1.765	1.717	1.737	1.702	1.737	1.155	1.702	0.041
	$c_{p,ck}$	4.149	3.936	4.302	3.471	3.263	3.277	2.833	2.738	3.040	1.514	3.252	0.659
	h_{comb}	27.717	27.971	27.439	27.153	26.768	26.497	27.001	26.559	26.835	26.998	27.094	0.235
Pns	$c_{p,db}$	1.333	1.436	1.286	1.382	1.056	1.318	1.387	1.413	1.413		1.336	0.013
	$c_{p,ck}$	2.018	1.836	1.647	1.437	3.151	2.234	3.475	2.206	2.074		2.231	0.449
	h_{comb}	30.087	30.996	30.864	31.104	29.955	30.082	31.322	31.386	30.412		30.690	0.316
Pp	$c_{p,db}$	1.532	2.435	1.381	1.368	1.412						1.626	0.209
	$c_{p,ck}$	1.966	–	0.468	0.794	–						1.076	0.621
	h_{comb}	28.950	29.033	28.850	27.741	28.356						28.586	0.292

where a_i is the value of a certain property in a fragment or sampling unit, a_L is the value in the whole batch, M_i is the mass of the fragment and N_F is the number of fragments.

In view of the above expressions, it is easy to deduce that the variance of the fundamental error is zero if, and only if, the sample is the whole batch, i.e., $M_m = M_L$, or the material is completely homogeneous, i.e., $a_i = a_L$, $i = 1,2,\ldots,N_F$.

The SGE is related to the distributional heterogeneity. The variance of the SGE, i.e., σ^2(SGE), cannot be calculated. However, because the relationship$0 \le \sigma^2(\mathrm{SGE}) \le \sigma^2(\mathrm{FE})$ has been verified [36], then the following relationship can be easily deduced:

$$\sigma^2(\mathrm{FE}) \le \sigma^2(\mathrm{SE}) \le 2\sigma^2(\mathrm{FE}). \tag{5}$$

Assuming that the sampling error follows a normal distribution, i.e., SE ~ $N(0,\sigma(\mathrm{SE}))$, we can ensure with a confidence level of 95% that:

$$|\mathrm{SE}| \le 1.96\sqrt{2}\sigma(\mathrm{FE}) = 1.96\sqrt{2}\sqrt{\left(\frac{1}{M_m} - \frac{1}{M_L}\right)HI_L}. \tag{6}$$

Finally, assuming that $M_m < M_L$,:

$$|\mathrm{SE}| \le 1.96\sqrt{\frac{2 \cdot HI_L}{M_m}} \tag{7}$$

Using the latest inequality, some useful bounds, with a confidence level of 95%, can be inferred for the SE and the mass of the sample:

1 If the mass of the sample is constant, the SE exhibits an upper bound of the maximum sampling error given by:

$$|\mathrm{SE}| \le \mathrm{SE}_{\mathrm{MAX}} = \sqrt{7.68\,\frac{HI_L}{M_m}}. \tag{8}$$

2 If a maximum sampling error is set, then the mass of the sample should be:

$$M_m \ge 7.68\,\frac{HI_L}{\mathrm{SE}^2_{\mathrm{max}}}. \tag{9}$$

More details about these results are available elsewhere [27].

2.4.2. Determination of confidence intervals

Another objective of this study was to approximate a_L, which is the value of a property in the entire batch. We assume that a_S is similar to the value of the property in the selected sample, i.e., a random variable with the following distribution:

$$a_S \sim N(a_L, \sigma(a_S)). \tag{10}$$

From the definition of the SE and Equation (5), an approximation of the variance was obtained:

$$\sigma^2(a_S) = \sigma^2(\mathrm{SE}) \cdot a_L^2 \le \frac{2}{M_m} HI_L \cdot a_L^2 \approx \frac{2}{M_m} HI_L \cdot a_S^2. \tag{11}$$

Finally, the value of a property in the entire batch, a_L, can be estimated as the mean of the experimental values, i.e., a realization of a_S, and confidence intervals for a_L can be obtained from the approximation of the variance of a_S.

3. Results and discussion

Values obtained during the TG/DSC tests of the different materials to obtain the specific heat of wood ($c_{p,db}$), the specific heat of

Table 4
Intrinsic heterogeneity of $c_{p,db}$, $c_{p,ck}$ and h_{comb} of different biomass materials.

	$c_{p,db}$	$c_{p,ck}$	h_{comb}
As	1.61×10^{-2}	1.00×10^{-2}	1.18×10^{-3}
Bp	1.20×10^{-2}	2.79×10^{-2}	3.67×10^{-3}
Gos	1.26×10^{-1}	9.48×10^{-2}	6.36×10^{-4}
Hs	2.03×10^{-3}	7.78×10^{-2}	1.53×10^{-3}
Op	1.19×10^{-2}	2.24×10^{-2}	1.11×10^{-4}
Pin	1.28×10^{-2}	5.61×10^{-2}	2.88×10^{-4}
Pns	6.72×10^{-3}	8.02×10^{-2}	2.99×10^{-4}
Pp	6.32×10^{-2}	3.57×10^{-1}	2.86×10^{-4}

Table 5
The minimum sample mass (expressed as number of sampling units) required to achieve a predetermined maximum sampling error for the determination of cp,db.

		Minimum sample size required to obtain a determined maximum error							
		As	Bp	Gos	Hs	Op	Pin	Pns	Pp
	HI_L	1.61×10^{-2}	1.20×10^{-2}	1.26×10^{-1}	2.03×10^{-3}	1.19×10^{-2}	1.28×10^{-2}	6.72×10^{-3}	6.32×10^{-2}
Maximum error	0.001	1.24×10^{5}	9.23×10^{4}	9.66×10^{5}	1.56×10^{4}	9.12×10^{4}	9.82×10^{4}	5.16×10^{4}	4.85×10^{5}
	0.005	4.95×10^{3}	3.69×10^{3}	3.86×10^{4}	6.24×10^{2}	3.65×10^{3}	3.93×10^{3}	2.06×10^{3}	1.94×10^{4}
	0.01	1.24×10^{3}	9.23×10^{2}	9.66×10^{3}	1.56×10^{2}	9.12×10^{2}	9.82×10^{2}	5.16×10^{2}	4.85×10^{3}
	0.05	4.95×10^{1}	3.69×10^{1}	3.86×10^{2}	6.24×10^{0}	3.65×10^{1}	3.93×10^{1}	2.06×10^{1}	1.94×10^{2}

Table 6
The maximum sampling error $SE_{\max}$ that corresponds to a given sample mass (expressed as number of sampling units) for the determination of $c_{p,db.}$

		Maximum error as a function of a given sample size							
		As	Bp	Gos	Hs	Op	Pin	Pns	Pp
	HI_L	1.61×10^{-2}	1.20×10^{-2}	1.26×10^{-1}	2.03×10^{-3}	1.19×10^{-2}	1.28×10^{-2}	6.72×10^{-3}	6.32×10^{-2}
Sample size	1	3.52×10^{-1}	3.04×10^{-1}	9.83×10^{-1}	1.25×10^{-1}	3.02×10^{-1}	3.13×10^{-1}	2.27×10^{-1}	6.97×10^{-1}
	10	1.11×10^{-1}	9.61×10^{-2}	3.11×10^{-1}	3.95×10^{-2}	9.55×10^{-2}	9.91×10^{-2}	7.18×10^{-2}	2.20×10^{-1}
	100	3.52×10^{-2}	3.04×10^{-2}	9.83×10^{-2}	1.25×10^{-2}	3.02×10^{-2}	3.13×10^{-2}	2.27×10^{-2}	6.97×10^{-2}
	200	2.49×10^{-2}	2.15×10^{-2}	6.95×10^{-2}	8.83×10^{-3}	2.14×10^{-2}	2.22×10^{-2}	1.61×10^{-2}	4.93×10^{-2}

coke ($c_{p,ck}$) and the heat of reaction (h_{comb}) are shown in Table 3, which also includes the mean and variance of the variables.

Table 4 presents the values of HI_L, that were calculated according to the method described in section 2. For calculations included in this table, fragment is assumed to be a dimensionless unit of mass, $M_i = 1$, so that the mass sample is represented as NF sampling units. That is to say, for each material the unit of mass stands for the sampling unit shown in Table 1.

Tables for any of the properties studied can be generated from the heterogeneity invariant so that the maximum error of a sample can be determined for a known sample size. The minimum sample size necessary to obtain the previously set maximum error of a sample can also be calculated. The minimum sample sizes necessary for a given maximum error and the maximum errors for a given sample size are presented in Table 5 and Table 6, respectively. The utility of these tables and examples of how they can be used are discussed elsewhere [28–31].

Following the methodology described in section 2.4, confidence intervals with a 95% confidence level for $c_{p,db}$, $c_{p,ck}$ and h_{comb} of each material were calculated. Table 7 shows the limits of these confidence intervals. The ranges are generally quite small, i.e., on the order of tenths, except for the h_{comb} of brassica pellets (Bp), the h_{comb} of hazelnut shells (Hs) and the $c_{p,ck}$ of poplar pellets (Pp), which exhibit ranges on the order of units.

An analysis of Table 3 reveals that it was not possible to determine the studied properties for all of the tested samples. The $c_{p,ck}$ of Sample #7 for almond shells (As), Samples #3, #5 and #6 for ground olive stones (Gos), Samples #1 and #10 for oak pellets (Op) and Samples #2 and #5 for poplar pellets (Pp) could not be determined. A notable difference was also observed between the minimum and maximum variance of the properties studied.

Table 7
Confidence intervals of the studied properties.

	$c_{p,db}$[J g^{-1} K^{-1}]	$c_{p,ck}$[J g^{-1} K^{-1}]	h_{comb}[kJ g^{-1}]
As	$1.51 \pm 1.77 \cdot 10^{-1}$	$2.39 \pm 2.35 \cdot 10^{-1}$	$29.07 \pm 9.22 \cdot 10^{-1}$
Bp	$1.49 \pm 2.02 \cdot 10^{-1}$	$2.48 \pm 5.12 \cdot 10^{-1}$	30.24 ± 2.27
Gos	$1.74 \pm 5.70 \cdot 10^{-1}$	$2.42 \pm 7.81 \cdot 10^{-1}$	$26.27 \pm 6.12 \cdot 10^{-1}$
Hs	$1.71 \pm 7.13 \cdot 10^{-2}$	$2.44 \pm 6.30 \cdot 10^{-1}$	31.01 ± 1.12
Op	$2.76 \pm 2.64 \cdot 10^{-1}$	$4.35 \pm 5.7 \cdot 10^{-1}$	$27.06 \pm 7.89 \cdot 10^{-1}$
Pin	$1.70 \pm 1.69 \cdot 10^{-1}$	$3.25 \pm 6.75 \cdot 10^{-1}$	$27.09 \pm 4.03 \cdot 10^{-1}$
Pns	$1.34 \pm 1.01 \cdot 10^{-1}$	$2.23 \pm 5.84 \cdot 10^{-1}$	$30.69 \pm 4.90 \cdot 10^{-1}$
Pp	$1.63 \pm 5.07 \cdot 10^{-1}$	1.08 ± 1.03	$28.59 \pm 5.99 \cdot 10^{-1}$

To relate the dissimilar values of the variance associated with average values that vary widely from each other, it is appropriate to compare the values of the coefficients of variation that allow an assessment of the magnitude of the dispersion from the mean. The coefficients of variation for each property of each of the materials are listed in Table 8.

Coefficients of variation (Table 8) for the specific heat of dry biomass and for the specific heat of coke are on the order of tenths. The specific heats of dry biomass are significantly lower, except for in the cases of almond shells (As) and ground olive stones (Gos). The coefficient of variation of the specific heat of coke for pine nut shells (Pns) reaches a value below the hundredths.

Because the measurements of the properties may exhibit temporary features, an additional analysis was performed to check for an underlying time-series structure. Because the TG/DSC tests were performed for each sampling unit, the derivation from each test of the values of the different properties, i.e., moisture, volatile, fixed carbon and ash, which were used in a previous work, and the specific heat of dry biomass, specific heat of coke and heat of reaction of coke, allows a comparison of the linear trend and random variation of the seven properties with previously published results [28].

Table 9 summarizes the results of statistical analyses applied to the sample data, i.e., Pearson correlation tests for the presence of a linear trend and the Ljung–Box test for the correlation time of random variation. The first two columns are used to verify the existence of a linear trend using the Pearson correlation coefficient and provide the corresponding p-value, respectively. The third and fourth columns show the p-values of the Ljung–Box test, which is a statistical hypothesis test used to test the null hypothesis that the residuals of a time series are uncorrelated.

Table 8
Coefficients of variation.

	Properties		
	$c_{p,db}$	$c_{p,ck}$	h_{comb}
As	0.135	0.107	0.036
Bp	0.122	0.186	0.068
Gos	0.376	0.333	0.088
Hs	0.049	0.296	0.041
Op	0.115	0.158	0.035
Pin	0.119	0.250	0.018
Pns	0.085	0.300	0.018
Pp	0.281	0.732	0.019

Table 9
Study of the linear trend and the random variation components for the studied properties.

		Pearson correlation		Ljung–Box test	
		coefficient	*p*-value	*p*-value for 1 lag	*p*-value for 2 lags
As	$c_{p,db}$	0.734	0.024	0.895	0.606
	$c_{p,ck}$	0.557	0.151	0.669	0.259
	h_{comb}	0.123	0.753	0.622	0.686
Bp	$c_{p,db}$	−0.642	0.243	0.117	0.248
	$c_{p,ck}$	−0.145	0.816	0.052	0.136
	h_{comb}	−0.725	0.166	0.402	0.186
Gos	$c_{p,db}$	0.274	0.475	0.289	0.484
	$c_{p,ck}$	0.048	0.928	0.545	0.276
	h_{comb}	0.645	0.061	0.455	0.561
Hs	$c_{p,db}$	0.584	0.099	0.290	0.317
	$c_{p,ck}$	−0.135	0.728	0.525	0.209
	h_{comb}	−0.870	0.002	0.147	0.349
Op	$c_{p,db}$	−0.531	0.115	0.265	0.534
	$c_{p,ck}$	−0.837	0.010	0.182	0.130
	h_{comb}	−0.826	0.003	0.287	0.556
Pin	$c_{p,db}$	−0.613	0.059	0.615	0.796
	$c_{p,ck}$	−0.899	0.001	0.475	0.441
	h_{comb}	−0.740	0.014	0.291	0.573
Pns	$c_{p,db}$	0.173	0.656	0.552	0.832
	$c_{p,ck}$	0.267	0.487	0.763	0.841
	h_{comb}	−0.222	0.566	0.955	0.046
Pp	$c_{p,db}$	−0.452	0.445	0.089	0.235
	$c_{p,ck}$	−0.744	0.466	0.068	0.153
	h_{comb}	−0.725	0.165	0.121	0.264

For a significance level of $\alpha = 0.05$, the values for oak pellets (Op) and pine pellets (Pin) exhibit a significant trend for the specific heat of coke and the heat of reaction. The values of the dry biomass specific heat for the almond shells (As) and the heat of reaction for hazelnut shells (Hs) also appears to exhibit a significant trend. These correlations seem to be random, because they appear in 6 of 24 cases studied, all with a limited number of tests.

After the trend has been removed, the Ljung–Box test detects the correlation in time. In the case of the heat of reaction for the pine nut shells, when considering two lags, we conclude that this relationship is irrelevant because the two lags only appear in a property of a material. The significance of this correlation in a single case suggests that this result is uncertain.

4. Conclusions

In this paper, samples obtained following the methodology described in [28] were investigated by TG/DSC analysis. The heat of reaction of the coke, the specific heat of the dry biomass and the specific heat of the coke were determined for some solid biofuels. Statistical analyses and other tests used in previous reports [29] to study the linear trend and the random variation of the properties were employed to analyze the results obtained during the experiments.

The lack of values for the specific heat of coke in samples of various materials indicates that the analysis has certain weaknesses and that the data are of limited reliability. This conclusion is supported by the variances and some intrinsic heterogeneities that lead to wide confidence intervals and high coefficients of variation in virtually all cases. As a result of the confidence intervals of the specific heats and the heats of reaction, we estimate that the average values can be employed in all cases, except for the specific heat of coke for pine pellets.

When comparing the linear trends and random variations of the properties of the eight materials listed in Table 9 with the results of the same test for other properties published elsewhere (Table 14 in previous work [28]), we observe that the materials with properties that suggest a structure-time series in a given case do not maintain this tendency in all cases. Therefore, these comparisons confirm that the correlations that appear are derived from random causes. The TG/DSC analyses presented in this paper and in previous works, as well as the process of extraction, reduction and sample testing, show neither linear trends nor correlations of time. This latter conclusion confirms the initial supposition of zero-dimensional samples.

Acknowledgments

The authors acknowledge financial support from the project 10DPI303006PR of the Xunta de Galicia. The work of Angeles Saavedra was partly supported by Xunta de Galicia project 10PXIB300068PR and by Spanish Ministry of Science and innovation projects MTM2008-03129 and MTM2011-23204. The work of Joaquín Collazo was funded by an Angeles Alvariño post-doctoral fellowship of the Xunta de Galicia.

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